

# FR2758431

## DEVICE OF ELECTROLUMINESCENT DISPLAY IN LAYER THIN AND A ALTERNATIVE EXCITATION AND ITS PROCESS OF REALIZATION

### CLAIMS

1. Device of electroluminescent display comprising an electroluminescent material made up of polymeric deposited in thin layer (15; 37) and at least two electrodes (12,13; 32,33) allowing the application of an electric field alternate to that electroluminescent material, characterized in that the two electrodes (12,13; 32,33) are laid out one beside other while letting remain a space between them, this space being occupied by the aforementioned electroluminescent material (15; 37).
2. Device of electroluminescent display according to claim 1, characterized in that the two electrodes (12,13; 32,33) allow the application of an electric field alternate of a given value in order to reveal a phenomenon of ionization under field in the aforementioned electroluminescent material.
3. Device of electroluminescent display according to one of the claims 1 or 2, characterized in that each electrode (32,33) having the shape of a comb, the electrodes are laid out of manner inter-digitée, the aforementioned space being made up by the way in defined lace by the teeth (34,35) of the electrodes in the shape of comb.
4. Device of electroluminescent display according to any of claims 1 to 3, characterized in that it comprises several pairs of electrode, each pair of electrode forming an unit of electroluminescent display (41,42,43,44).
5. Device of electroluminescent display according to claim 4, characterized in that each unit of electroluminescent display (41,42,43,44) has a particular electroluminescent material so that the device of display constitutes a polychromatic screen.
6. Device of electroluminescent display according to any of claims 1 to 5, characterized in that the electrodes (12,13; 32,33) are made up in a material chosen among metallic materials or doped semiconductor materials with low resistivity.
7. Device of electroluminescent display according to any of claims 1 to 6, characterized in that the polymeric component the aforementioned electroluminescent material (15; 37) is selected among the polyvinylcarbazole, polyphenylenevinylene and polythiophene.
8. Device of electroluminescent display according to any of claims 1 to 7, characterized in that the polymeric component the aforementioned electroluminescent material (15; 37) contains a dye chosen among coumarin, rhodamine and the DCM.
9. Device of electroluminescent display according to any of claims 1 to 8, characterized in that the electrodes and the electroluminescent material are laid out on a support (11; 31; 40) realized in a material chosen among glass, polycarbonate or polyethylene.
10. Method for realization of a device of electroluminescent display in thin layer, characterized in this qu it comprises the following steps
  - the deposit, on a face of a support (11) of at least two electrodes (12,13) intended to allow the application of an electric field with an electroluminescent material,
  - the deposit, on the aforementioned face of the support (11), of a layer of polymeric constituting the

electroluminescent material (15) so that the aforementioned applied electrical field causes an effect of electroluminescence in the aforementioned electroluminescent material.

11. Proceeded according to claim 10, characterized in that the step of deposit of the two electrodes (12,13) comprises a phase of deposit of a continuous conductive layer (10) and a phase of engraving of the aforesaid the continuous conductive layer (10) to form the two electrodes (12,13).

12. Proceeded according to one from the claims 10 or 11, characterized in that the electroluminescent material (15) is obtained by deposit of a solution of polymeric and evaporation.

13. Proceeded according to claim 12, characterized in that the deposit of the electroluminescent material (15) is carried out by serigraphy.

## DESCRIPTION

The present invention relates to a device of electroluminescent display in thin layer and to alternative excitation and its method for realization.

The flat display screens can be used as devices of display in numerous fields. They can be carried out according to different technical. One thus finds screens with liquid crystals, plasma display screens, and screens electroluminescent.

The electroluminescent screens present, compared to the other types of flat screens, the benefit to implement technical very solid. From the point of view of visualization, the elements of image (or pixels) of an electroluminescent screen are net and contrast is excellent with a very large angle of sight

The displaying information is done also, particularly for the dashboards of the indicating automobiles, screens in the stations and the airports, the bill-posters of certain portable instruments, by the use of a coloured layer being used as masque of light. The display is carried out starting from lamps placed at rear of the screen. Such a structure requires a mechanical mounting complexes because of the brittleness of the elements to assemble and the difficulty resulting of the assembly. It would be thus advantageous to have another device of display, in particular of the electroluminescent type for the qualities enumerated above.

Figure 1 represents, in a schematic way, an electroluminescent device according to the known art.

This device includes/understands a transparent substrate 1, out of glass or plastic, which supports a transparent electrode 2 for example out of indium oxide. A metallic electrode 3, for example out of aluminium, is laid out compared to the transparent electrode 2.

The space ranging between electrodes 2 and 3 is filled with a luminescent semiconductor material 4 which can be polymeric. The device represented functions under continuous tension, the transparent electrode 2 playing the part of anode and electrode 3 playing the part of cathode. When the device is energized, the indium oxide constituting electrode 2 is positively polarized. Positive loads (holes) and negative loads (electrons) are injected into the polymeric one. These loads recombine to form an excited state (exciton) which returns to the fundamental state by emitting a photon. The color of the emitted light according to the designated direction by an arrow on figure 1 depends on the structure of the polymeric one. The choice of the luminophore determines the length of wave of emission.

The polymeric electroluminescent one can be polyvinylcarbazole doped by a dye such as coumarin 515, as that is described in the article "Blue light-emitting diodes with doped polymers" of E. GAUTIER and Al, published in Synthetic Metals, pages 197-200, flight. 81, 1996.

Electroluminescent presenting a superposition of layers adjacent of that of figure 1 and excited devices by an alternating voltage are also known.

This device of the known art, where the electroluminescent material is incorporated between control electrodes, requires a precise control of the thickness of polymeric electroluminescent. Moreover, cathode (the metallic electrode) must be generally deposited vacuum.

The present invention was particularly conceived in order to have technical simple of realization of electroluminescent devices of display. This device of display comprises, on an insulating substrate, at least a pair of electrode laid out laterally, preferably interdigitated and delimiting each one a selected pattern. Preferably, at least the space ranging between the electrodes of the aforesaid the pair is covered with an electroluminescent layer into polymeric semiconductive organic, containing a dye optionally. An applied alternating voltage between the electrodes of a same pair creates, in electroluminescent material, a parallel electrical field with the substrate. The invention allows an easy manufacture since it requires only one conductive deposit, an engraving of the electrodes and an electroluminescent material deposit of thickness noncritical by technical serigraphy or very other of painting. The electroluminescent material is ionizable under field, which removes the electrochemical reactions to the interfaces, causes degradation.

The invention thus has as an object a device of electroluminescent display comprising an electroluminescent material made up of polymeric deposited in thin layer and at least two electrodes allowing the application of an electric field alternate to that electroluminescent material, characterized in that the two electrodes are laid out one beside other while letting remain a space between them, this space being occupied by the aforementioned electroluminescent material. Preferably, each electrode having the shape of a comb, the electrodes are laid out of manner interdigitée, the aforementioned space being made up by the way in defined lace by the teeth of the electrodes in the shape of comb.

The device can comprise several pairs of electrode, each pair of electrode forming an unit of electroluminescent display. In this case, each unit of electroluminescent display can have a particular electroluminescent material so that the device of display constitutes a polychromatic screen.

The invention also has as an object a method for realization of a device of electroluminescent display in thin layer, characterized in that it comprises the following steps

- the deposit, on a face of a support of at least two electrodes intended to allow the application of an electric field with an electroluminescent material,
  - the deposit, on the aforementioned face of the support, of a layer of polymeric constituting electroluminescent material so that the aforementioned applied electrical field causes an effect of electroluminescence in the aforementioned electroluminescent material.
- Preferably, the deposit of the two electrodes comprises a phase of deposit of a continuous conductive layer and a phase of engraving of the aforesaid the continuous conductive layer to form the two electrodes.

The invention will be included/understood better and of other benefits and features will appear with the reading of the description which will follow, given as nonrestrictive example, accompanied by the annexed figures among which

- figure 1 is a schematic sight and out of transverse cut of a device of electroluminescent display according to the known art,
  - figure 2 is a schematic sight and out of transverse cut of a device of electroluminescent display according to the present invention,
  - the figures 3A with 3rd are illustrative of a method for realization according to the present invention, making it possible to obtain the device of electroluminescent display represented on figure 2,
  - figure 4 represents an electroluminescent device according to the present invention and including/understanding two electrodes inter-digitées, each electrode having the shape of a comb,
  - figure 5 represents a polychromatic electroluminescent screen according to the present invention.
- The electroluminescent device of figure 2 represents a basic structure of the present invention. It includes/understands a support 11, a first electrode 12 and one second electrode 13 deposited on support 11. Electrodes 12 and 13 are laid out one beside other and form between them a channel 14 whose width is for example about 1  $\mu\text{m}$ . A layer of luminous material 15 is then deposited on the structure by covering electrodes 12 and 13 and the channel 14. This luminous material is polymeric semiconductive deposited by wet way, i.e.

in a solvent, the solvent being then evaporated either naturally, or of forced manner, by centrifugation.

The device of figure 2 functions in AC current. The applied tension between electrodes 12 and 13 has a frequency chosen in the range going from 50 to 5000 Hz. The tension of injection varies linearly with the width of the channel 14.

Under the effect of a sufficiently high, induced electrical field by the applied tension enters electrodes 12 and 13, of the loads of opposite signs (positive and negative) are created spontaneously in the polymeric one: C is ionization under field. This electrical field is about  $600 \text{ V} > m$  in the case of a polymeric composition made up of polyvinylcarbazole and coumarin 515 at a rate of 10! in ground compared to the polymeric one. In each geometric configuration, and each polymeric particular considered, one can define an electrical threshold of field from which this phenomenon of ionization appears. The electrical loads created in the polymeric one are distributed on both sides channel the positive loads on a side and the negative loads of other according to the sign of the applied tension. As the device is fed in alternating voltage, the applied tension changes sign and the loads are then led, under the effect of the electrical field, towards the side opposite of the channel compared to that which they occupied previously. The loads of opposite signs cross and can then recombine, as in the devices of the former art, to form an excited state (exciton) which returns to the fundamental state by emitting a photon. The color of the emitted light depends on the polymeric composition. This composition can be either polymeric in solution in which a dye (the luminophore) is dissolved or polymeric on which the dye is linked chemically (by organic synthesis). In the case already quoted of the polymeric composition polyvinylcarbazole-coumarin 515, X let us net vinylcarbazole can be linked with net coumarin, X there + y being equal with 1 and being able there to go from 0,03 to 0,3. The light generated by electroluminescent effect is emitted perpendicularly with support 11. If this support is transparent, the light is emitted in the two directions as the arrows drawn on figure 2 show it.

Support 11 can be a substrate of glass or plastic. If this support is not transparent, the light is emitted only by the transparent face into polymeric. The polymeric one must be transparent with the emitted light to avoid its reabsorption. For example, the polyvinylcarbazole absorbs in ultraviolet ray. The dissolved or linked dye with this polymeric determines the color of the emitted light. Coumarin emits in the blue one to 490 Nm, rhodamine 6G emits out of orange with 550 Nm and the DCM emits into red to 620 Nm.

Like transparent support, ordinary glasses are appropriate, as well as polycarbonate. The thickness of a rigid support can be 1 to 5 Meters. Flexible supports are also operable. It can then be a question of polycarbonate or film polyethylene of 0,1 Meters.

The consumption of the device is linked with the resistance characteristics and of capacitance of the circuit. For a channel of 1 cm of long, the consumption of the device is worth 10 MW typically. A typical example of realization of this circuit now will be described in relation to the figures 3A with 3rd. Support 11 is for example an ordinary, rectangular glass plate (20 mm X 40 mm) and of 1 mm of thickness, previously degreased and cleaned of any organic impurity in a bath of ultrasounds containing a detergent. On support 11, one deposits to see the figure 3A) a thin layer 10 of aluminium, 120 Nm of thickness, per vacuum evaporation, for a pressure of  $1,33.10^{-4} \text{ Pa}$  (10-6 Torr), at a speed of 4 Nm a second. Pendent evaporation, the support is maintained at an upper temperature at 100 °C in order to ensure a good contact of aluminium on glass by eliminating any trace from steam. One deposits then, on the thin layer of aluminium 10, a layer 20 of positive resin photosensitive in ultraviolet light. It can be a question of a resin of the series Microposit STR 1000 of SHIPLEY, deposited by centrifugation with 1000 turns/minute. Its thickness is of 400 Nm.

As shown in the figure 3B, the layer of resin 20 is insulated by a light beam delivered by a laser with argon of 10 uW of power to 364 Nm front the microscope objective of focusing on the layer of resin. The focal spot makes 500 Nm diameter and the beam laser sweeps the surface of the layer of resin at a speed of 300 um/seconde. The scanning determines the form of the etched portion 21 of

the resin which will provide a channel in the present case, but which could provide other forms such as a comb as it further will be seen.

The insulated resin is developed pendent 30 seconds in a bath of Microposit MF-319 (SHIPLEY). One obtains the structure represented with the figure 3C where the layer of resin 20 comprises an etched zone 22.

With the following step, the portion of the layer of aluminium not covered with resin then is attacked chemically in phosphoric acid at 50 °C pendent 90 seconds. With the exit of this step, the initial layer of aluminium is transformed into two electrodes 12 and 13 laid out coast at coast and separated by the channel 14 from 1,2 µm from width as that is visible on the figure 3D.

The excess resin is then dissolved in ordinary acetone. The electroluminescent material can then be deposited. For that, a polymeric drop of composition, including/understanding polyvinylcarbazole with 35 g/l in chlorobenzene and coumarin 515 at a rate of 10% in ground compared to polymeric, is deposited per centrifugation with 1000 turns/minute on the channel 14. This formulation leads to one thickness from polymeric 15 of 250 Nm (see the figure 3rd). The electrical contacts with the electrodes can be obtained by means of a conductive resin (paste with the silver).

In this device according to the present invention, one does not use an upper metallic counter-electrode as for the former art (electrode 3 of figure 1). This electrode, obtained by vacuum evaporation, is always delicate to realize

In order to produce a screen of display of "macroscopic" size (several cm<sup>2</sup> for example), it is advisable to give to the electrodes the form combs and to lay out them in order to imbricate them one in the other one, each tooth of an electrode in the shape of comb lying between two consecutive teeth of the other electrode in the shape of comb.

It is what is represented on the figure 4 which is a sight of top of such a device. This figure watch a support 31 supporting two electrodes 32 and 33 in the shape of comb. Each tooth 34 of electrode 32 (except the last one) lies between two consecutive teeth 35 of electrode 33. Inversely, each tooth 35 of electrode 33 (except the last one) lies between two consecutive teeth 34 of electrode 32. The length of channel 36 between electrodes 32 and 33 is thus considerably increased since this channel is now consisted the way in defined lace by the interdigitated electrodes 32 and 33. Electrodes 32 and 33 are preferably extended by zones of contact 38 and 39, respectively, to allow the application of an electric field. The distance between two adjacent teeth 34 and 35 is adjacent 1 µm. Polymeric electroluminescent the 37 is merely painted over the combs.

Once the etched metallic electrodes according to the pattern chosen, the polymeric one can be painted without particular precautions on the electrodes.

The thickness of polymeric electroluminescent is indifferent as soon as it exceeds the thickness of the electrode, which is always the case by serigraphy. It is also possible to deposit a drop of polymeric in solution, the volatile solvent of the solution evaporating spontaneously.

An engraving of electrodes per microlithography UV through a masque is also possible (see the work "Positive photoresist, materials and processes" of DEFOREST, McGraw-Hill, 1983). It makes it possible to be freed from the laser and to carry out more complex patterns. This technical applique for supports of low size to 30 cm.

It can be judicious to use, on a same device of display, several different polymeric compositions allowing the emission of lights of different colors. It is what figure 5 represents which is a sight of top of a polychromatic electroluminescent screen. This screen includes/understands four electroluminescent units 41, 42, 43 and 44 of the type of figure 4 with electrodes out of comb interdigitées formed on support 40. As example, unit 41 can emit a green color, unit 42 a blue color, unit 43 a red color and unit 44 an yellow color. Any soluble dye presenting a high output of photoluminescence can use the polymeric composition.

Like source of operable dyes, one can quote the catalogue of the dyes laser EXCITON, Dayton, Ohio 45437, the United States.

Each electroluminescent unit 41, 42, 43 and 44 of figure 5 can, have respectively connected one of its electrodes, 411, 421, 431 and 441 of manner common to an electrode of general ground 401.

The application of a suitable tension on each other electrode 412, 422, 432, 442 allows the emission of a light of particular color.

For these devices according to the present invention, the choice of material of the electrodes is not very critical because the injection of current does not take place actually of the electrode towards the polymeric one. Indeed, the loads are injected by ionization under field. Like electrode material, one can choose any stable metal

(gold, silver, copper, aluminium) like very semiconductive doped with low resistivity (indium oxide, silicon, polyaniline, polypyrrole or polythiophene). The choice of polymeric semiconductive is less critical than in the devices of the former art. Its conveying character of electrons (N) or holes (p) is of no importance. The polymeric semiconductive one must be good insulating and must have a good mobility (N or p). The polyvinylcarbazole used in electrophotography fills these criteria.

One can also use a derivative of polyphenylenevinylene or polythiophene or very other polymeric semiconductive such as those described in "Handbook of conducting polymers" of Skotheim, published at Marcel

Dekker in 1986.

The brightness of the devices obtained is substantial. It can reach 105 cd/m<sup>2</sup> in blue light and 10 times more in green light. At comparable surface, it can be a question of an upper profit with 104 compared to the solutions of the former art, type describes on figure 1. The reason of this profit is ascribable with the good mobility of the unipolar carriers (p) in the polyvinylcarbazole like with the good balance of injection of carriers of the two signs.

The stability of the device proposed by the invention is strongly increased compared to the solutions of the known art. The lifespan can be increased by 3 orders of magnitude. The balance of injection of the carriers is indeed carried out by ionization under field, which reduced losses by Joule effect. Moreover, no permanent current forwards between the electrodes and the polymeric one, which removes the electrochemical reactions occurring with the interfaces and which represent the first cause of degradations of the electroluminescent devices of the known art as the article to it "Electrode testifies interfaces effects one indium-chock-oxide polymer/metal light emitting diodes" by E. GAUTIER and Al, published in the Appl review. Phys.

Lett. 69 (8) of August 19, 1996, pages 1071-1073.

These devices of electroluminescent display can be perfectly integrated in self-contain microsystems possessing a function of display (in portable telephony for example). They can be used in the dashboards of automobiles and to carry out large-sized bill-posters for indication in the nodes of communication (highways, airports, stations).